PLANETARY PHYSICS I:

THE PHOTOIONIZATION OF ATOMIC OXYGEN

A. Dalgarno,* R.J.W. Henry* and
A. L. Stewart*†

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GEOPHYSICS CORPORATION OF AMERICA Bedford, Massachusetts

^{*}On leave of absence from the Department of Applied Mathematics, The Queen's University of Belfast, Belfast, N. Ireland.

[†]At the Stanford Research Institute, Menlo Park, California, for the session 1963-1964.

ABSTRACT

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The formulation of a Hartree-Fock approximation for the final states of a transition involving the ejection of an outer or an inner shell electron from all ground state configurations $1s^2 \ 2s^2 \ 2p^q$ is presented and the cross sections for the photoionization of atomic oxygen by radiation at wavelengths longer than 25 Å are calculated.

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A. Dalgarno, R.J.W. Henry and A. L. Stewart

1. Introduction

The photoionization cross sections of atomic oxygen are basic atomic parameters of fundamental importance in the quantitative understanding of the ionosphere. An accurate calculation at the spectral head has been carried out by Bates and Seaton (1949) but the only values at shorter wavelengths, where ejection of the inner shell electrons is energetically possible, are the approximate estimates of Dalgarno and Parkinson (1960) and of J. Cooper (1963, unpublished).

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2. The Hartree-Fock Equations

We assume that the wave functions of the initial and final states of the transition may be represented by linear combinations of Slater determinants, the elements of which are normalized orbitals. The wave functions are characterized by the quantum numbers L and S of respectively the total orbital and total spin angular momenta and the transitions with which we are concerned may be described by

$$1s^{2} 2s^{2} 2p^{q} 2s+1L_{i} \rightarrow 1s^{2}2s^{2}2p^{q-1} \in \ell^{2s+1}L_{f}$$
 (1)

for the ejection of an outer shell electron and by

$$1s^{2}2s^{2}2p^{q}^{2s+1}L_{i} \rightarrow 1s^{2}2s2p^{q} \in \ell^{2s+1}L_{f}$$
 (2)

for the ejection of an inner shell electron, ϵ rydbergs being the energy of the ejected electron.

We assume that the core of the final state is unaffected by the continuum $\epsilon\ell$ electron. Then the Hartree-Fock equations for the radial wave functions of the core electrons may be constructed following standard procedures (cf. Slater 1960). For the ls and 2s electrons of the configuration $1s^22s^22p^{q-1}$, they are respectively

$$\left\{ \frac{d^{2}}{dr^{2}} + \left[\frac{2}{r} \quad Z - Y^{0}(1s,1s) - 2Y^{0}(2s,2s) - (q-1)Y^{0}(2p,2p) \right] - \lambda_{1s,1s} \right\} P(1s|r) + \left\{ \frac{2}{r} Y^{0}(1s,2s) - \lambda_{1s,2s} \right\} P(2s|r) + \frac{q-1}{3r} Y^{1}(1s,2p) P(2p|r) = 0.$$
(3)

and

$$\left\{ \frac{d^{2}}{dr^{2}} + \frac{2}{r} \left[Z - 2Y^{0}(1s,1s) - Y^{0}(2s,2s) - (q-1)Y^{0}(2p,2p) \right] - \lambda_{2s,2s} \right\} P(2s|r) + \left\{ \frac{2}{r} Y^{0}(1s,2s) - \lambda_{2s,1s} \right\} P(1s|r) + \frac{q-1}{3r} Y^{1}(2s,2p) P(2p|r) = 0.$$
(4)

where

$$Y^{k}(n\ell, n'\ell') = \frac{1}{r^{k}} \int_{0}^{r} P(n\ell|\rho)P(n'\ell'|\rho)\rho^{k} d\rho$$

$$+ r^{k+1} \int_{r}^{\infty} P(n\ell|\rho)P(n'\ell'|\rho) \frac{1}{2^{k+1}} d\rho$$
(5)

For the 2p electron of the configuration $(1s^22s2p^q)^{2S}1^{+1}L_1$, the radial equation is

$$\left\{ \frac{d^{2}}{dr^{2}} - \frac{2}{r^{2}} + \frac{2}{r} \left[z - 2Y^{0}(1s,1s) - Y^{0}(2s,2s) - (q-1) Y^{0}(2p,2p) - \frac{2a-2q(q-1)}{25q} Y^{2}(2p,2p) \right] - \lambda_{2p,2p} \right\} P(2p|r) + \frac{2}{3r} Y^{1}(1s,2p)P(1s,|r) + \frac{q-b}{3qr} Y^{1}(2s,2p) P(2s|r) = 0.$$
(6)

where a and b are coefficients given in Table 1.

We form the final state by adding an electron to the unperturbed core, any off-diagonal interactions between core parent states being ignored. For ejection of the outer shell electron, the allowed values

Table 1

Values of the coefficients a and b of Equation (6).

q	2S+1 _L	^{2S} 1+ _{L1}	a	b
0.6	1 _s	² s	0	0
1.5	² P	3 _P	0	-1
		1 _P	0	3
2.4	3 _P	⁴ P	-3	-2
		² P	-3	4
3	⁴ s	⁵ s	- 9	-3
		³ s	- 9	5

of ℓ are 0 and 2 and the radial equations for $P(\epsilon s | r)$ and $P(\epsilon d | r)$ are respectively

$$\left\{ \frac{d^{2}}{dr^{2}} + \frac{2}{r} \left[z - 2Y^{0}(1s,1s) - 2Y^{0}(2s,2s) \right] \right. \\
\left. - (q-1) Y^{0}(2p,2p) \right] + \epsilon \right\} P(\epsilon s | r) \\
+ \left\{ \frac{2}{r} Y^{0}(1s,\epsilon s) - \lambda_{1s,\epsilon s} \right\} P(1s | r) \\
+ \left\{ \frac{2}{r} Y^{0}(2s,\epsilon s) - \lambda_{2s,\epsilon s} \right\} P(2s | r) \\
+ \frac{2}{r} \frac{(3q-3-b')}{18} Y^{1}(2p,\epsilon s) P(2p | r) = 0$$
(7)

and

$$\frac{d^{2}}{dr^{2}} - \frac{6}{r^{2}} + \frac{2}{r} \left[Z - 2Y^{o}(1s,1s) - 2Y^{o}(2s,2s) \right] - (q-1) Y^{o}(2p,2p) - \frac{a''}{105} Y^{2}(2p,2p) + \epsilon P(\epsilon d|r) + \frac{2}{5r} Y^{2}(1s,\epsilon d) P(1s|r) + \frac{2}{5r} Y^{2}(2s,\epsilon d) P(2s|r) + \frac{2}{r} \left[\frac{(6q-6-b'')}{90} Y^{1}(2p,\epsilon d) + \frac{(21q-21-c'')}{490} Y^{3}(2p,\epsilon d) \right] P(2p|r) = 0$$
(8)

where b', a", b" and c" are coefficients given in Table 2.

For ejection of the inner shell 2s electron, the allowed value of ℓ is 1 and the radial equation for $P(\epsilon p | r)$ for the configuration

Values of the coefficients b' of Equation (7), and a", b", c" of Equation (8). For $\ell=0$, a" = b" = c" = 0 and for $\ell=2$; b' = 0.

Table 2

			$\ell = 0$				
q	2S+1 ₁	L _i .	2s ₁ +1 _{L1}	2S+1 _{Lf}	:	b'	
1	2 _P		¹ s	² s		0	
2	3 _P		² P	³ P		- 3	
3	⁴ s		3 _P	⁴ P		- 6	
4	3 _P		⁴ s	3 s		15	
			² D	3 _D		- 3	
			2 P	3 _P		- 3	
5	2 _{P}		3 _P	² P		12	
			¹ D	² D		0	
			¹s	2 _S		0	
6	¹ s		2 _P	¹ P		9	
			<i>l</i> = 2				
q	^{2S+1} L _i	^{2S} 1 ⁺¹ L ₁	25	+1 _{Lf}	a"	b"	c ¹¹
1	² P	¹ s	· · · · · · · · · · · · · · · · · · ·	² _D	0	0	0
2	³ p	² P		³ _D	-21	24	- 21
				3 _P	21	0	-105
3	⁴ s	3 p		⁴ P	-21	36	- 84

Table 2 (continued)

q	2S+1 _L	2S ₁ +1 _L 1	^{2S+1} L _f	a"	b"	c"
4	3 _P	⁴ s	³ D	0	30	105
		² D	3 _D	0	3	- 57
			3 _P	0	27	- 63
			³ s	0	42	- 63
		2 _P	³ D	0	9	- 21
			3 _P	0	- 3	- 63
5	$^2\mathbf{P}$	3 _P	² D	-21	69	84
			^{2}P	21	33	- 42
		¹ D	² D	9	9	- 36
			2 _P	-21	33	- 42
			² s	-42	48	- 42
		¹ s	² D	0	0	0
6	¹ s	2 _P	¹ P	-21	114	- 21

$$1s^{2} 2p^{q}(^{2S+1}L_{i}) \in p^{2S}1^{+1}L_{f,2s}^{2S+1}L_{f}^{1} is$$

$$\left(\frac{d^{2}}{dr^{2}} - \frac{2}{r^{2}} + \frac{2}{r}\left[Z - 2Y^{o}(1s,1s) - Y^{o}(2s,2s)\right] - q Y^{o}(2p,2p) - \frac{\alpha}{25} Y^{2}(2p,2p)\right] + \epsilon \right) P(\epsilon p|r)$$

$$+ \frac{2}{r}\left(\frac{1}{3} Y^{1}(1s,\epsilon p) P(1s|r) + \frac{6-\beta}{36} Y^{1}(2s,\epsilon p) P(2s|r)\right)$$

$$+ \frac{q-\gamma}{6} Y^{o}(2p,\epsilon p) P(2p|r) + \frac{10q-\delta}{150} Y^{2}(2p,\epsilon p) P(2p|r)$$

$$- \lambda_{2p,\epsilon p} P(2p|r) = 0$$
(9)

where α , β , γ and δ are coefficients given in Table 3.

In deriving the radial equations it has been assumed that the orbitals are mutually orthogonal. This involves no loss of generality for $P(\epsilon s|r)$ and $P(\epsilon d|r)$ but it may be an added restriction in the determination of $P(\epsilon p|r)$. However, because the core is not perturbed by the continuum electron, the assumption does not lead to any contradiction despite the fact that the final configuration involves two open shells of the same symmetry.

The orthogonality requirement suffices to determine the off-diagonal Lagrange multipliers $\lambda_{1s, \in s}$, $\lambda_{2s, \in s}$ and $\lambda_{2p, \in p}$. Thus from (3) and (7)

$$\lambda_{1s, \in s} = -\frac{b!}{18} (2p | \frac{2}{r} Y^{1}(1s, 2p) | \in s)$$
 (10)

Table 3 $\label{eq:Values} Values \ of \ the \ coefficients \ \alpha, \ \beta, \ \gamma \ and \ \delta \ of \ Equation \ (9) \ .$

q	^{2S+1} L _i	^{2S} 1 ⁺¹ L _f	^{2S+1} L _f	α	β	Υ	δ	
0	¹s	² _P	¹ P	0	18	0	0	
		3 _D	² D	1	12	- 5	4	
		3 _P .	² P	- 5	12	7	-20	
1	² _P	3 _S	² s	10	12	- 5	- 50	
	,	¹ D	² D	1	0	7	16	
		¹ P	² P	- 5	0	· - 5	40	
		⁴ D	³ D	- 1	10	-4	- 4	
		⁴ P	3 _P	5	10	-4	-40	
2	³ P	⁴ s	³ s	-10	10	14	-40	
		² D	³ D	- 1	2	5	32	
		² P	³ P	5	2	5	50	
		³ s	³ s	-10	2	-4	50	
3	⁴ s	⁵ P	⁴ P	0	9	-3	-30	
		³ P	⁴ P	0	3	5	50	
		⁴ D	³ D	1	10	-2	-20	
		⁴ P	³ D	- 5	10	-2	-20	
4	3 _P	⁴ s	³ s	10	10	-2	-20	
		² D	³ D	1	2	-2	61	
		² _P	3 _P	- 5	2	16	25	
		² s	³ s	10	2	-2	-20	
		3 _D	² D	- 1	12	-1	-10	

Table 3 (continued)

q	2S+1 _L i	2S ₁ +1 _L _f	^{2S+1} L _f	α	β	γ	δ
5	2 _P	3 _P	2 _P	5	12	- 1	-10
		³ s	² s	-10	12	- 1	-10
		¹ D	² D	- 1	0	- 1	62
		¹ P	² P	5	0	- 1	-10
		¹ s	² s	-10	0	35	-10
6	¹ s	² P	$^{1}{}_{P}$	Ö	18	0	0

from (4) and (7)

$$\lambda_{2s, \in s} = -\frac{b!}{18} (2p | \frac{2}{r} Y^{1}(2s, 2p) | \in s)$$
 (11)

and from (6) and (9)

$$\lambda_{2p,\epsilon p} = \frac{1}{3} \left(1s \left| \frac{2}{r} Y^{1}(1s,\epsilon p) \right| 2p \right) - \frac{1}{3} (1s \left| \frac{2}{r} Y^{1}(1s,2p) \right| \epsilon p \right)$$

$$+\frac{b-q}{6q} (2s|\frac{2}{r} Y^{1}(2s,2p)|\epsilon p)$$

$$+\frac{6-\beta}{36} (2s|\frac{2}{r} y^{1}(2s, \epsilon p)|2p)$$

$$+\frac{q-\gamma-6}{5}(2p|\frac{2}{r}Y^{0}(2p,2p)|\epsilon p)$$

$$+\frac{10q^{2}-12q(q-1)-6qc+12a-\delta q}{150q} (2p|\frac{2}{r} Y^{2}(2p,2p)|\epsilon p)$$
 (12)

3. The Photoionization Cross Sections

The cross sections for the photoionization of an atomic system with an ionization potential of I rydbergs by radiation of wavelength λ Å is given by (cf. Bates 1946),

$$a_{\lambda} = \frac{8.56 \times 10^{-19}}{\omega_{i}} \quad (I + \epsilon) \text{ S cm}^{2}$$
 (13)

where

$$I + \epsilon = \frac{911.754}{\lambda} , \qquad (14)$$

 ω_i is the statistical weight of the initial state and S is the absolute multiplet strength. If the initial state is labelled by a superscript i and the final state by a superscript f and the continuum wave function $P(\in \ell_f | r)$ is normalized to an amplitude $(\Pi \in \frac{1}{2})^{-\frac{1}{2}}$, then

$$S = \prod_{\substack{\text{passive} \\ \text{electrons}}} \left| \int_{0}^{\infty} P^{i}(n\ell|r) P^{f}(n\ell|r) dr \right|^{2} \left(\mathcal{N} \right) \sigma^{2}$$
 (15)

where $\mathcal{C}(\mathcal{U})$ is the relative multiplet strength and

$$\sigma^2 = \frac{1}{4\ell_>^2 - 1} \left| \int_0^\infty P^i(n\ell_i|r) P^f(\epsilon \ell|r) r dr \right|^2 \qquad (16)$$

where $\ell_{>}$ is the greater of ℓ_{i} and ℓ . Expression (16) arises in the dipole length formulation. In the dipole velocity formulation, the matrix element

$$\left| \int_{0}^{\infty} P^{i} \left(n\ell + 1 \middle| r \right) P^{f}(\epsilon \ell \middle| r) r dr \right|$$
 (17)

is replaced by

$$\frac{2}{(I+\epsilon)} \int_{0}^{\infty} \left\{ \frac{\ell+1}{r} P^{f}(\epsilon \ell | r) - P^{f'}(\epsilon \ell | r) \right\} P^{i}(n\ell+1|r) dr$$
 (18)

and

$$\left| \int_{0}^{\infty} P^{i}(n \ell - 1 | r) P^{f}(\epsilon \ell | r) r dr \right|$$
 (19)

by

$$\frac{2}{1+\epsilon} \left| \int_0^\infty \left\{ \frac{\ell}{r} \ P^f(\epsilon \ell | r) + P^{f'}(\epsilon \ell | r) \right\} P(n\ell-1|r) dr \right|, \qquad (20)$$

the primes denoting differentiation with respect to r.

The relative multiplet strengths $\mathcal{S}(\hat{\mathcal{H}})$ may be obtained by a straightforward application of Racah algebra (cf. Rohrlich 1959). They are given in Table 4 for transitions involving the ejection of an outer shell electron. The relative multiplet strengths corresponding to the ejection of an inner shell electron are all unity.

Table 4 . Relative multiplet strengths \mathcal{S} $\left(p^{q}SL_{i}; p^{q-1}(S_{1}L_{1})\ell SL_{f}\right)$

	·				
q	2S+1 _L	^{2S} 1 ⁺¹ L ₁	Ł	2S+1 _L f	& (M)
1	² P	¹ s	0	² s	6
	$^2\mathbf{p}$	¹ s	2	² D	60
2	3 _P	2 _P	0	3 _P	18
	3 _P	2 _P	2	³ D	135
				3 _p	45
3	4 _S	3 _P	0	4 _P	12
	⁴ s	3 _P	2	4 _P	120
4	3 _P	⁴ s	0	³ s	12
		² D	0	³ D	15
		2 _P	0	³ P	9
	3 _P	4 _s	2	³ D	120
	3 _P	² D	2	3 _D	105/2
				3 _P	135/2
				³ s	30
	³ _P	² P	2	3 _D	135/2
				3 _P	45/2
5	2 _P	3 _P	0	2 _P	18
		¹ D	0	² D	10
		¹ s	0	² s	2

Table 4 (continued)

ď	^{2S+1} L _i	2S ₁ +1 _L	l	2S+1 _L	$\mathscr{S}(\mathcal{M})$
	² p	3 _P	2	² D	135
				² P	45
		¹ D	2	² D	35
				² P	45
				² s	20
		1 _S	2	² D	20
6	¹s	² _P	0	1 _P	6
	¹ s	2 _P	2	¹ p	60

4. Numerical Procedures

The core integrals in (7), (8) and (9) were evaluated analytically using the representations of the core orbitals of 0⁺(1s²2s²2p³) ⁴S, ²P, ²D and 0⁺(1s²2s2p⁴) ⁴P, ²P obtained by Roothaan and Kelly (1963), and the remaining integrals were evaluated numerically. An iterative procedure was used to solve the equations, the first solution being obtained by ignoring the exchange integrals. The iterations were continued until each of the dipole length and the dipole velocity matrix elements had converged to three significant figures. In general, the dipole velocity matrix element converged much more rapidly than the dipole length matrix element.

The method adopted by Bates and Seaton (1949) of varying the off-diagonal Lagrange parameters until orthogonality is obtained is not convenient for automatic computation and we computed then directly at each stage of the iteration, a technique which has the further advantage that it provides a powerful computational check. Thus when the iteration procedure has converged, the overlap integrals of $P(\epsilon s | r)$ with P(2s | r) and P(1s | r) and of $P(\epsilon p | r)$ with P(2p | r) should have vanished.

Some difficulty was encountered in the determination of $P(\epsilon p \mid r)$ because of the slow convergence of the straightforward iterative procedure. The difficulty was resolved by adopting for the next stage of the iteration the arithmetic average of the two previous solutions.

5. Results and Discussion

The cross sections for the individual transitions

$$0(1s^2 2s^2 2p^4)^{3}P + h\nu \rightarrow 0^{+}(1s^2 2s^2 2p^3)^{4}S, ^{2}D, ^{2}P + e^{-}$$
(21)

and

$$0(1s^2 2s^2 2p^4) ^3P + h\nu \rightarrow 0^+(1s^2 2s 2p^4) ^4P, ^2P + e^-$$
 (22)

are important in predicting the electron temperature in the ionosphere (Dalgarno, McElroy and Moffett 1963) and in predicting the intensities of ionic emission lines arising from fluorescence (Dalgarno and McElroy 1963). The results corresponding to both the dipole length (curve A) and dipole velocity (curve B) formulations are shown in Figures 1 to 5 and the cross sections for the sum of processes (21) and (22) are shown in Figures 6 and 7.

At the spectral head at 910 Å, we obtain cross sections of respectively 2.7 x 10^{-18} cm² and 3.4 x 10^{-18} cm² in the length and velocity formulations, each of which is about 25% larger than that computed by Bates and Seaton (1949). The discrepancies probably arise from the different forms employed for the discrete orbitals.

It is not possible to decide which of the length and velocity cross sections is the more accurate. For the photoionization of neon, a comparison of the theoretical (Seaton 1954) and measured values (Ditchburn 1960) shows that the velocity values are more accurate at the spectral head and at short wavelengths and the length values are more accurate

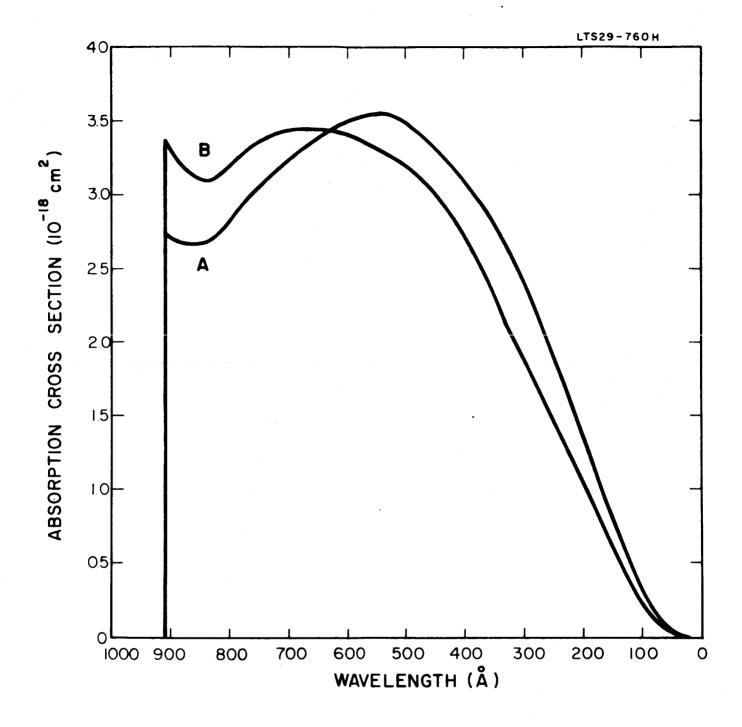


Figure 1.
$$O(^{3}P) + h\nu \rightarrow O^{+}(^{4}S) + e^{-}$$
.

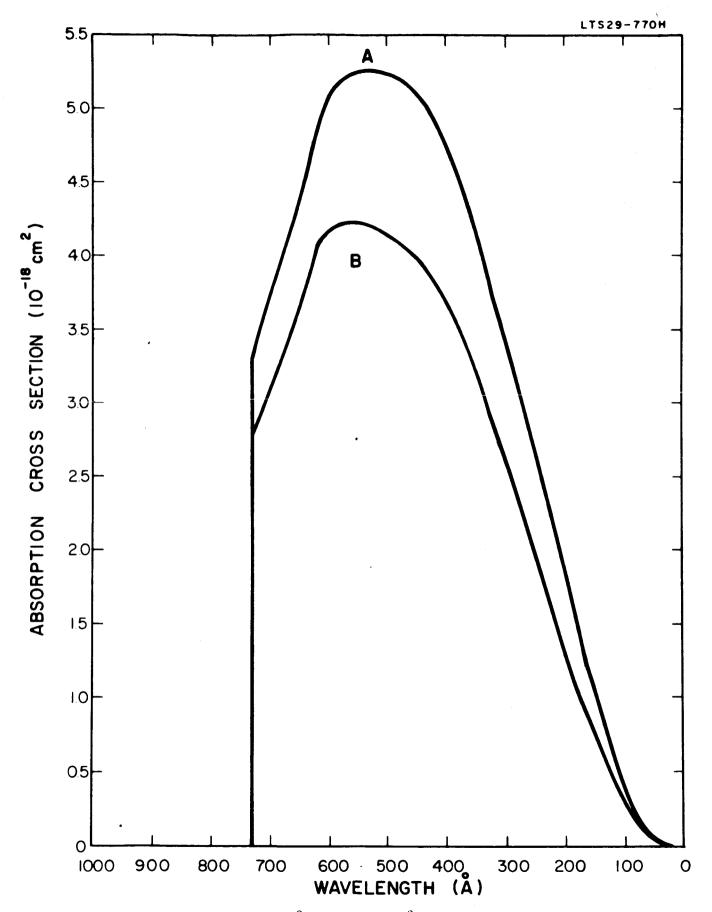


Figure 2. $O(^{3}P) + h\nu \rightarrow O^{+}(^{2}D) + e^{-}$.

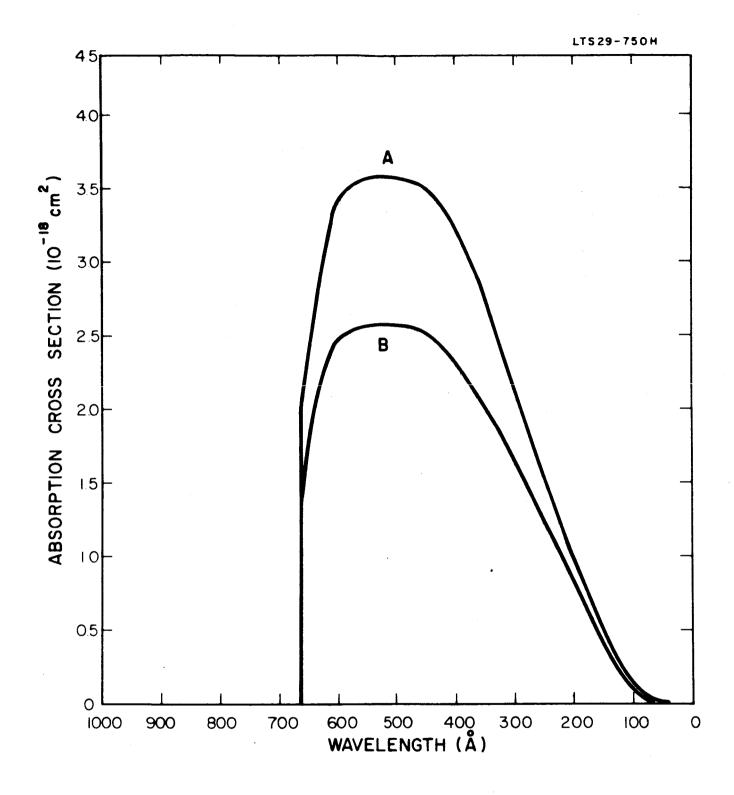


Figure 3. $O(^{3}P) + h_{\nu} \rightarrow O^{+}(^{2}P) + e^{-}$.

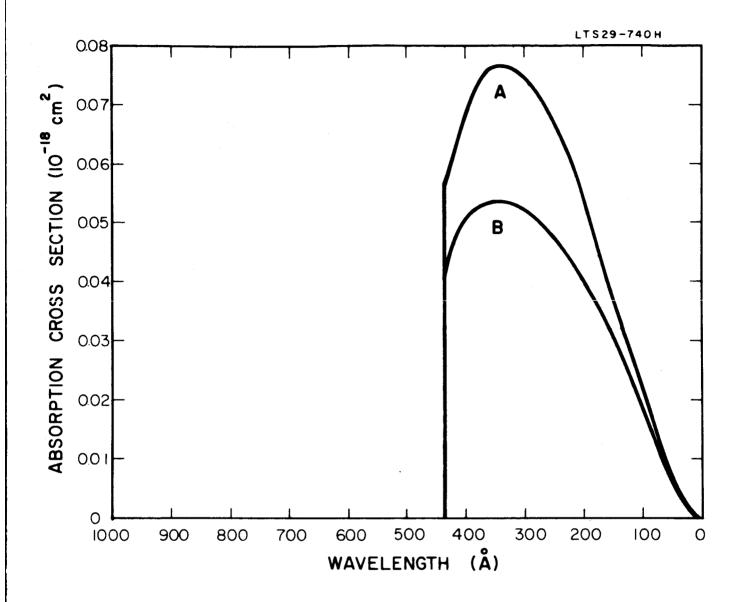


Figure 4.
$$O(^{3}P) + h_{V} \rightarrow O^{+}(^{4}P) + e^{-}$$
.

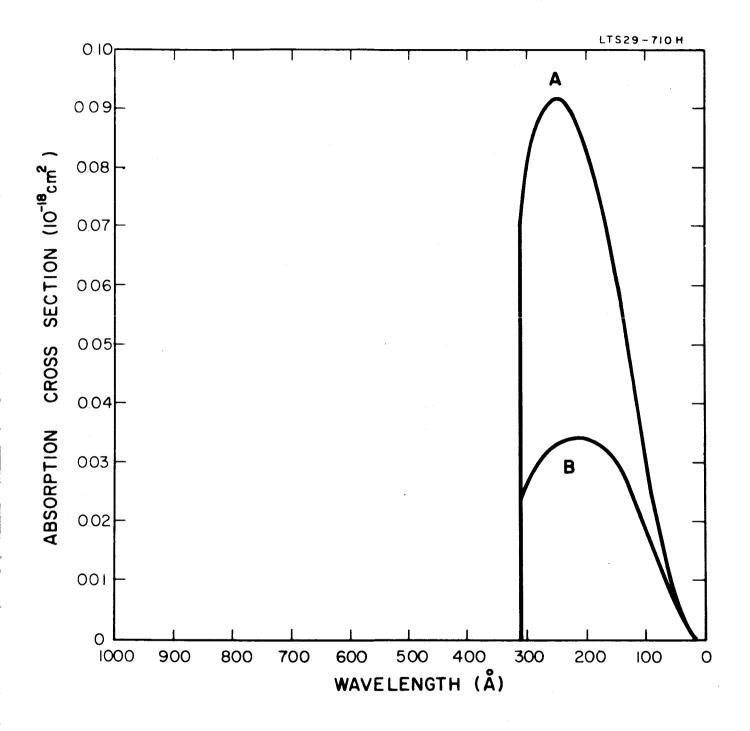


Figure 5. $O(^{3}P) + h_{\nu} \rightarrow O^{+}(^{2}P) + e^{-}$.

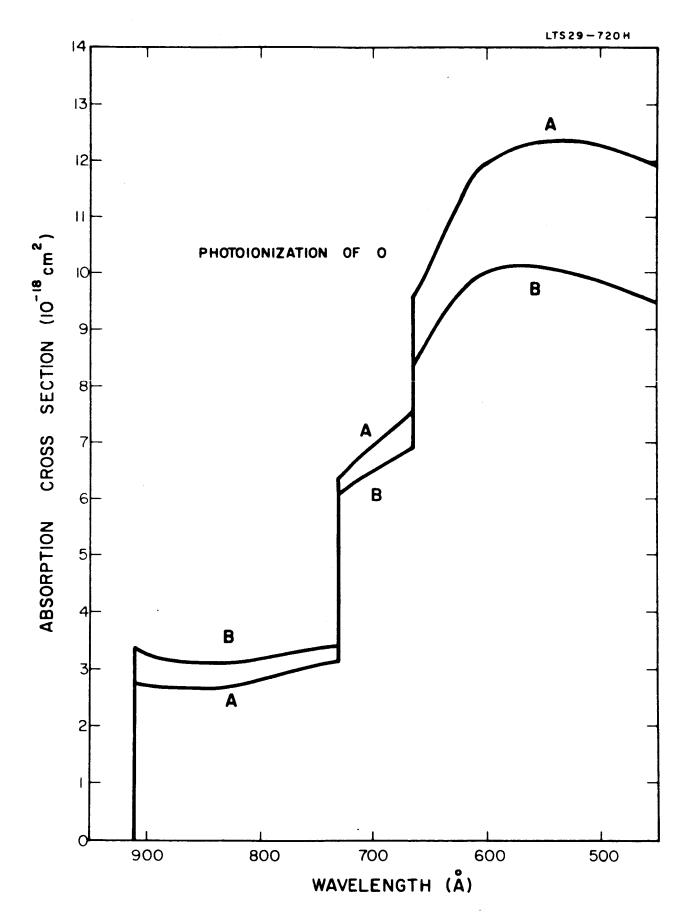


Figure 6. Absorption cross sections, λ 1000 - λ 500.

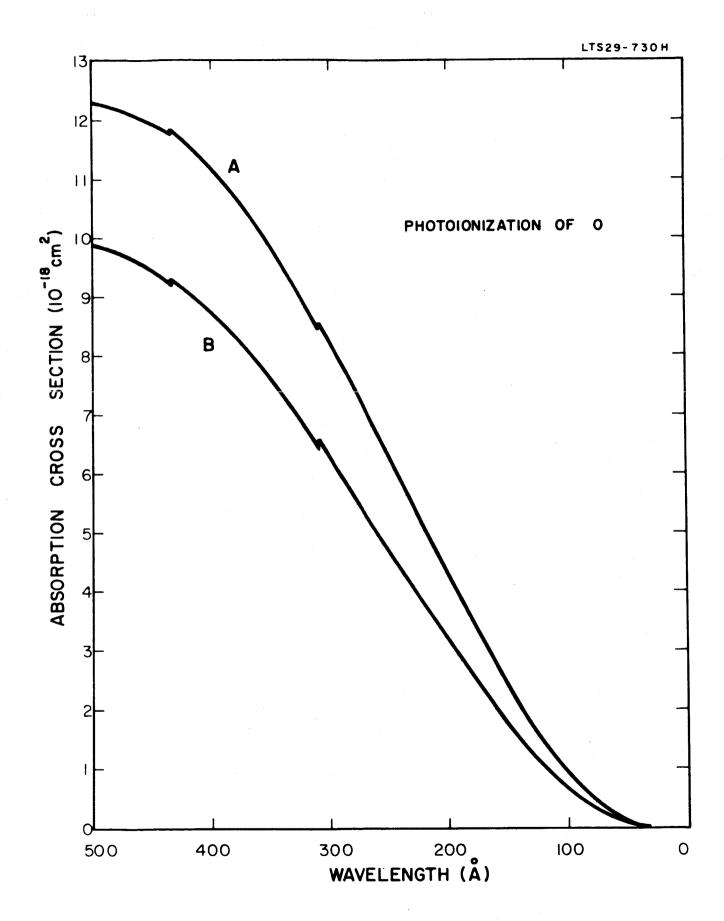


Figure 7. Absorption cross sections, λ 500 - λ 0.

at intermediate wavelengths, but there seems little reason to expect a similar behaviour for oxygen. Because the velocity formulation should be the more accurate at short wavelengths (Dalgarno and Lewis 1956) and because we found that it converged much more rapidly in the iterative process, we regard the velocity cross sections as the more reliable. Except at short wavelengths, the differences between the length and velocity cross sections are never greater than 25% and this percentage may be accepted as a measure of the accuracy of the dipole velocity results.

We include a table of cross sections appropriate to the most important of the solar lines observed by Hall, Damon and Hinteregger (1963). (Table 5)

Recent discussions of the formation of the ionosphere have been based upon the cross sections given by Dalgarno and Parkinson (1960) whose values are generally about 40% larger than those in the table.

Table 5

Cross sections appropriate to some important solar lines

λ(Å)	a \lambda	λ(Å)	$^{a}_{\lambda}$
283	5.72(-18)*	584.3	1.01(-17)
303.8	6.34(-18)	610	9.96(-18)
335	7.18(-18)	625	9.60(-18)
368.1	8.11(-18)	629.7	9.45(-18)
465.2	9.64(-18)	770.4	3.30(-18)
500	9.87(-18)	789	3.22(-18)
520	9.98(-18)	834	3.09(-18)
554	1.01(-17)	875	3.19(-18)

^{* 5.72} x 10⁻¹⁸cm²

Acknowledgements

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Legends

- Figure 1. The absorption cross sections as a function of wavelength for the transition $O(^3P) + h\nu \rightarrow O^+(^4S) + e^-$. Curves A and B refer to the dipole length and velocity transition matrix elements respectively.
- Figure 2. The absorption cross sections as a function of wavelength for the transition $0(^3P)$ + $h\nu$ + $0^+(^2D)$ + e^- .

 Curves A and B as in Figure 1.
- Figure 3. The absorption cross sections as a function of wavelength for the transition $0(^3P)$ + $h\nu \rightarrow 0^+(^2P)$ + e^- .

 Curves A and B as in Figure 1.
- Figure 4. The absorption cross section as a function of wavelength for the transition $0(^3P)$ + $h\nu \rightarrow 0^+(^4P)$ + e^- . Curves A and B as in Figure 1.
- Figure 5. The absorption cross section as a function of wavelength for the transition $0(^3P) + h\nu \rightarrow 0^+(^2P) + e^-$.

 Curves A and B as in Figure 1.
- Figure 6. The absorption cross sections for the sum of processes (21) and (22) as a function of wavelength λ 1000 λ 500 Å. Curves A and B as in Figure 1.
- Figure 7. The absorption cross sections for the sum of processes (21) and (22) as a function of wavelength λ 500 λ 0 Å. Curves A and B as in Figure 1.